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Effect of Intermolecular Interaction on the Characteristics of Organic Light Emitting Diodes with TPBB Derivatives

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We synthesized four new emitting materials of triphenylamine derivatives, 1,3,5-tris (4′-(1″-phenyl-benzimidazol-2″-yl)phenyl)amine (TPBB), MeO-TPBB, Br-TPBB, and Bu-TPBB, and investigated the effects of substituent on their intermolecular interaction and luminescence characteristics. UV-vis absorption and photoluminescence (PL) spectra of the TPPB derivatives measured in dilute solution were almost the same but, in solid state, the PL spectra exhibited large differences depending on the substituent. Especially, the PL spectra of Br-TPPB redshifted remarkably in solid state. We also prepared electroluminescent devices with the multilayer structure of [ITO/NPB (50 nm)/EML (30 nm)/TPBI (20 nm)/Alq3 (10 nm)/LiF (1 nm)/Al] using one of the TPBB derivatives as an emitting layer. The TPBB derivatives showed much different electroluminescence (EL) characteristics depending on the nature of the substituent. This suggests that each substituent present different degree of intermolecular electronic interaction in the TPBB derivatives.

Keywords 1,3,5-tris(4′-(1″-phenyl-benzimidazol-2″-yl)phenyl)amine; heavy atom effect; intermolecular interaction; organic light emitting diodes

Introduction

Organic light emitting diode (OLED) is now considered as a prime display device of the next generation because of its potential for thin, light-weight, low-power, and also flexible displays [1,2]. Although much progress has been made over the past two decades, researches for new materials with high luminescent efficiency and stability are still going on [3,4] with the efforts to develop ingenious device fabrication techniques [5,6].

In search of a new emitting material, many derivatives of luminescent molecules were synthesized with various functional substituents [7] because the photoelectronic and physical properties can be modified depending on the substituent

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Address correspondence to Prof. Young Chul Kim, Department of Chemical Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Korea. E-mail: kimyc@khu.ac.kr groups. It has been reported that the optical and electrical properties of conjugated materials are dependent on the nature of the substituents (electron-donating or electron-withdrawing) of conjugated systems as well as on the π-conjugation length and interchain distance of the conjugated segments [8,9]. In addition to the effects of electron-donating or -withdrawing substituents on the electronic structure of the molecule, the effects of substituents on the intermolecular interaction has also been studied [10]. The emitting materials which have different intermolecular interaction tend to show different photo- and electro-luminescence characteristics [11]. Ku *et al.* has confirmed that intermolecular dipole interactions are detrimental to the photoluminescence efficiency in solid state, retarding their uses as solid state emitters in OLED devices [12]. They also reported that, in solid state, a slight red-shift of the absorption and emission maxima occurred, compared with those obtained in dilute solution.

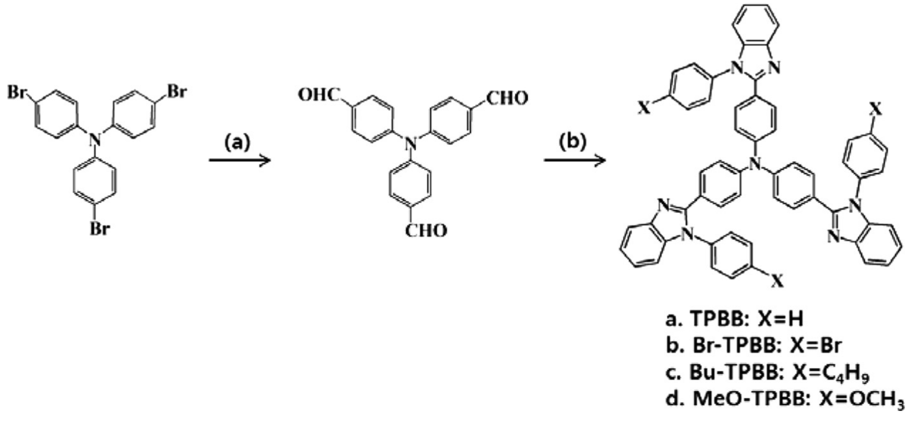
In this work, we synthesized four new emitting materials of triphenylamine derivatives, 1,3,5-tris(4′-(1″-phenyl-benzimidazol-2″-yl)phenyl)amine (TPBB), MeO-TPBB, Br-TPBB, and Bu-TPBB, and investigated the effects of substituents on their intermolecular interaction and luminescence characteristics.

Experimental

Synthesis of the TPBB Derivatives and Fabrication of OLEDs

As presented in Scheme 1, the TPBB derivatives were synthesized from the reaction between 4,4′,4″-nitrotribenzaldehyde and N-phenyl-2,3-phenylenediamine in the presence of $Na_2S_2O_5$ with an yield of 95%. Methoxy, bromine, and n-butyl groups were substituted at the para-positions of the phenyl rings to prepare the compounds b–d.

The OLED devices were fabricated on the pre-patterned indium-tin-oxide (ITO)-coated glass substrates with a sheet resistance of $10\,\Omega/\square$. The size of pre-patterned ITO coated glass substrates was $3 \times 3\,\text{cm}^2$ and each substrate has four pixels with the active area of $3 \times 3\,\text{mm}^2$. The substrate was sequentially cleaned with trichloroethylene, acetone, deionized water, and isopropyl alcohol in an ultrasonic bath each for about 10 min followed by rinsing in deionized water. The cleaned substrate was treated with oxygen plasma for 2 min at a power of 600 W.



Scheme 1. Synthetic route to the TPBB derivatives: (a) BuLi/DMF, THF, −78°C; (b) N-phenyl-2,3-phenylenediamine, $Na_2S_2O_5$, DMF, 150°C.

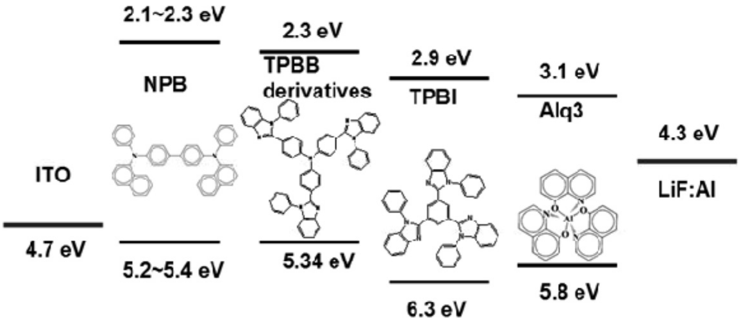


Figure 1. Energy band diagram of the materials used in the OLED devices.

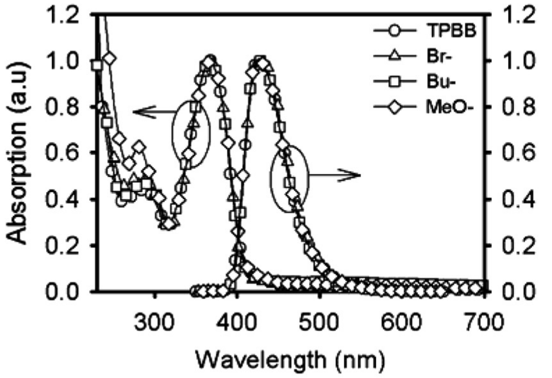
Four OLED devices with the multilayer structure of [ITO/NPB (50 nm)/EML (30 nm)/TPBI (20 nm)/Alq3 (10 nm)/LiF (1 nm)/Al] were prepared by using one of the TPBB derivatives as an emitting layer (EML). In the devices, N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) was used as a hole transport layer (HTL), 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) as a hole blocking layer (HBL), tris-(8-hydroxyquinoline) aluminum (Alq_3) as an electron transport layer (ETL), and the bilayer of lithium fluoride (LiF) and aluminum (Al) as a cathode. All organic and metal layers were deposited by thermal evaporation under $\sim 10^{-6}$ torr onto the ITO substrate and the deposition rates were 1.0, 0.1, $3 \sim 4$ Å/s for the organic, LiF, and Al layers, respectively. The intersection area of cathode and anode defines the active area of the device. The energy band diagram of the devices is shown in Figure 1.

Measurements

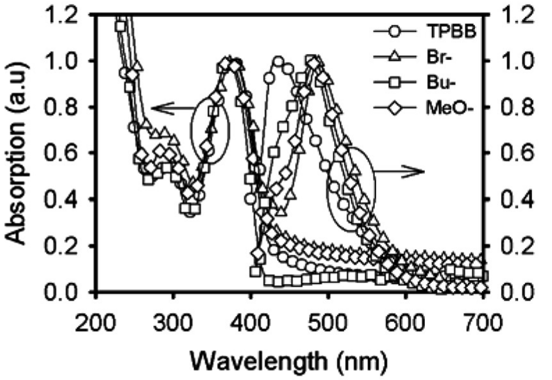
UV-vis absorption and photoluminescence (PL) spectra were measured using an Agilent 8453 UV-visible spectrophotometer and a PTI QuantaMaster™ spectrofluorometer, respectively. Cyclic voltammograms were recorded on a Bioanalytical System Bas 100B in 0.1 M Bu_4NPF_6/CH_2Cl_2 solution with a platinum working electrode, a platinum auxiliary electrode, and a saturated Ag/AgCl reference electrode. Differential scanning calorimetric analysis (DSC) were performed on a Perkin Elmer N536-0003 at a scan rate of 10°C/min under nitrogen atmosphere. Electroluminescence characteristics of the devices were studied by using a JBS I-V-L 300 EL characterization system equipped with a Keithley 2400 sourcemeter.

Results and Discussion

We measured the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the TPBB derivatives in order to investigate the effect of substituent on the electronic states of the materials. HOMO level was calculated by using the oxidation potential onset measured from cyclic voltammograms and LUMO level by adding the optical bandgap to the HOMO level. However, all of the TPBB derivatives showed almost the same HOMO and LUMO levels of 5.34 and 2.30 eV, respectively, without reference to the substituent. It implies that the Br, n-Bu, and MeO substituents could hardly alter the energy levels of TPBB although they have different electron donating ability.



(a)

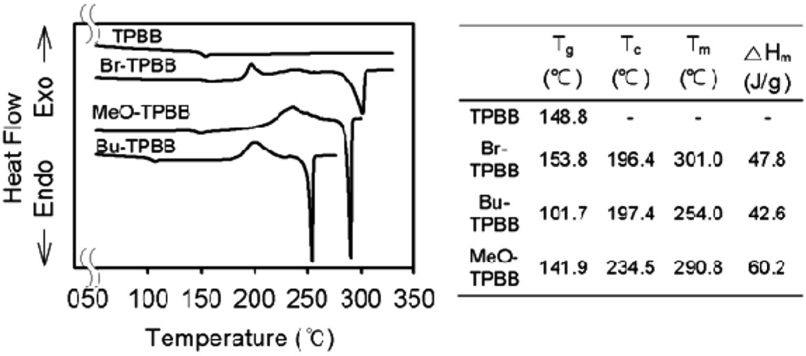


(b)

Figure 2. Normalized UV-vis absorption- and PL-spectra of the TPBB derivatives measured (a) in the solution and (b) in the solid states.

Normalized UV-vis absorption and PL spectra of the four new luminescent materials measured in dilute toluene solution and thin solid film states are shown in Figure 2. The absorption peak wavelengths of the materials measured in solution state are located at practically the same wavelength of 368 nm and also the PL peaks fell within 425–430 nm. On the other hand, the materials in solid state exhibited significantly different PL spectra while the absorption spectra were much similar. The PL peak wavelengths of Br-, MeO-, and Bu-TPBB in solid state shifted remarkably to the longer wavelengths than in solution state. The PL peak wavelengths of TPBB, Br-TPBB, Bu-TPBB, and MeO-TPBB in solid state were observed at 432, 489, 478, and 484 nm, respectively. The degree of redshift was dependant on the substituent although the substituents could not change the bandgap of TPBB. Therefore these spectral shifts in the solid state spectra are attributed to the different degree of intermolecular interactions provided by the different substituents.

DSC thermograms of the materials could give some information on their molecular mobilities in melt state and the intermolecular interactions in solid state as shown in Figure 3. The materials were cooled from 350°C at a rate of 10°C/min after the initial heating in order to erase the previous thermal history. During the



	T_g (℃)	T_c (℃)	T_m (℃)	$\triangle H_m$ (J/g)
TPBB	148.8	-	-	-
Br-TPBB	153.8	196.4	301.0	47.8
Bu-TPBB	101.7	197.4	254.0	42.6
MeO-TPBB	141.9	234.5	290.8	60.2

(a) (b)

Figure 3. (a) DSC thermograms of the TPBB derivatives and (b) summary of thermal characteristics.

second heating scan, TPBB showed only glass transition but the Br-, Bu-, and MeO-TPBB showed the crystallization and melting behavior as well as glass transition. This suggests that the substitution increased the mobility of TPBB and the derivatives with substituent could have intermolecular interactions strong enough to form crystals. As indicated by the heat of fusion (ΔH_m), MeO-TPBB has the highest crystallizability, followed by Br-TPBB and Bu-TPBB.

We fabricated the OLEDs with the multilayer structure of [ITO/NPB (50 nm)/EML (30 nm)/TPBI (20 nm)/Alq3 (10 nm)/LiF (1 nm)/Al] using one of the TPBB derivatives as an emitting layer in order to confirm the effect of intermolecular interaction on the electroluminescence performances. Previously, we fabricated the OLED devices with various structures using TPBB as an emitting layer and obtained the best EL properties with abovementioned structure, which will be reported elsewhere. Figure 4 shows the current density-voltage-luminance (J-V-L) characteristics and luminous efficiencies of the devices with the TPBB derivatives. The device with unsubstituted TPBB showed the best performance with the maximum luminance of 10,000 cd/m^2 and a luminous efficiency of 2.9 cd/A at a current density of 100 mA/cm^2 but the devices with Br-, Bu-, and MeO-TPBB gave lower luminance and luminous efficiency.

As shown in Figure 5, the emission of Br-, Bu-, and MeO-TPBB redshifed not only in the solid state photoluminescence but also in the electroluminescence spectra. The effect of substituent is considered to make the TPBB molecules more mobile so that the aggregates are formed from several neighboring molecules to have stronger intermolecular interaction. DSC study of the materials supports this tendency. It is generally understood that excimer (M^*M) or exciplex (M^*N) can be formed by strong interactions between the molecular segments in excited state (M^*) and the same molecules (M) or a different molecules (N) in the ground state, respectively, when aggregated. And the emission spectrum from the excimer or exciplex has a broad peak or shoulder in the longer wavelength region [13]. In this work, neither a broad peak due to an excimer emission was observed, nor the redshift of the TPBB derivatives reached that of the excimer or exciplex but, the redshift is considered to originate from the increased intermolecular interaction in the densely packed molecules, which caused by the molecular mobility provided by the substituent.

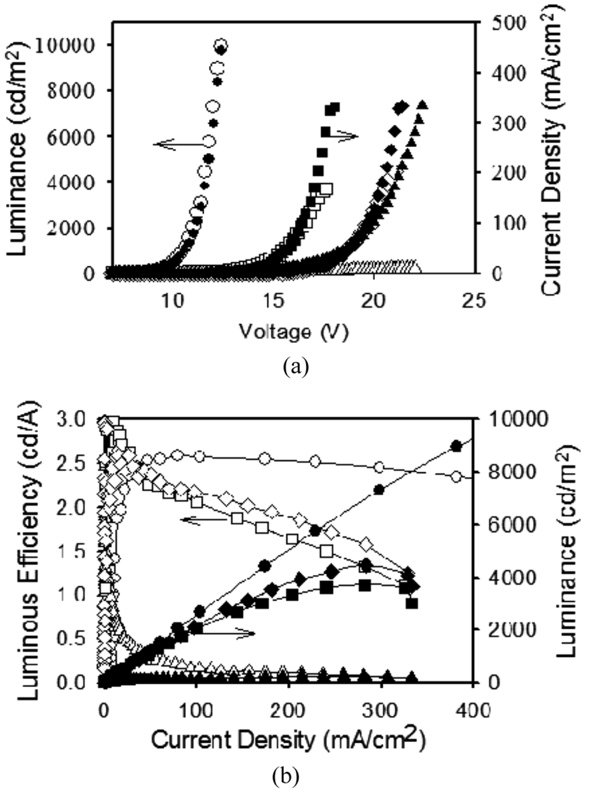


Figure 4. (a) The current density-voltage-luminance (J-V-L) characteristics and (b) luminous efficiency of the devices fabricated with the TPBB derivatives (○: TPBB, △: Br-TPBB, □: Bu-TPBB, ◇: MeO-TPBB).

In the case of the Br-TPBB based device, however, it is not enough to explain the remarkable redshift and significant decrease of luminance and efficiency as just the result of the increased intermolecular interaction. The low fluorescence quantum yield of the Br-substituted compound can be ascribed to the high non-radiative

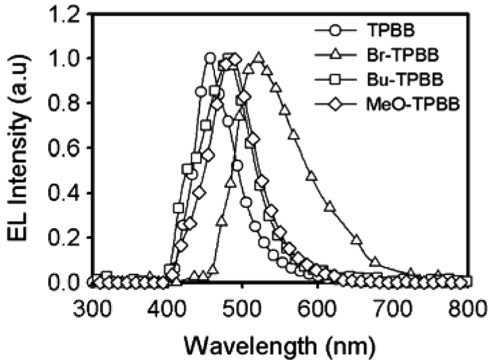


Figure 5. EL-spectra of the devices fabricated with the TPBB derivatives.

Table 1. Summary of EL characteristics of the OLEDs fabricated with TPBB derivatives

Emitting layer	Max luminance [cd/m^2]	Turn on voltage [V]^a	Luminous efficiency [cd/A]^b	E.Q.E [%]^b	EL λ_{max} [nm]^b	CIE Coordinates [X, Y]^b
TPBB	10000 at 440 mA/cm^2	8	2.93	1.7	444	0.15, 0.15
Br-TPBB	230 at 200 mA/cm^2	16	0.17	0.05	511 520	0.33, 0.53
MeO-TPBB	4500 at 280 mA/cm^2	16	2.17	0.9	486	0.16, 0.27
Bu-TPBB	3700 at 280 mA/cm^2	12	2.05	1.1	481	0.16, 0.21

[a] Defined as the voltage required to reach a luminance of 100 cd/m^2.
[b] Measured at 100 mA/cm^2.

deactivation that occurs during intersystem crossing from S_1 to T_1, which is often referred to as the "heavy atom effect" observed in the presence of bromine atom [14,15]. The EL characteristics of all the devices are summarized in Table 1.

The reason for the great performance of the device with TPBB is that the molecular mobility of TPBB is not enough to form aggregates. On the other hand, the TPBB derivatives with Bu- and MeO-substituents can gain enough molecular mobility for a dense packing to have a stronger intermolecular interaction, leading to the decreased EL performances and the redshifted spectra. Although Br-TPBB has low molecular mobility comparable to TPBB, it has strong intermolecular attraction force enough to crystallize upon heating. The poor EL characteristics of Br-TPBB are considered to result from both the strong intermolecular attraction force and the heavy atom effect of bromine.

Conclusion

We studied the effects of intermolecular interaction on the electroluminescence properties of the OLED devices fabricated with the TPBB derivatives. The TPBB derivatives substituted with Br, n-butyl, and methoxy groups showed enhanced molecular mobility than unsubstituted TPBB resulting in more dense molecular packing. Therefore the PL spectra of solidified Br-, Bu-, and MeO-TPBB redshifted compared with those obtained in solution state. Unsubstituted TPBB showed a better EL performance than the substituted TPBBs and the substituted TPBBs exhibited poor EL properties due to the increased intermolecular interaction. The heavy atom effect of bromine also deteriorated the EL performance of the device fabricated with Br-TPBB.

Acknowledgments

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